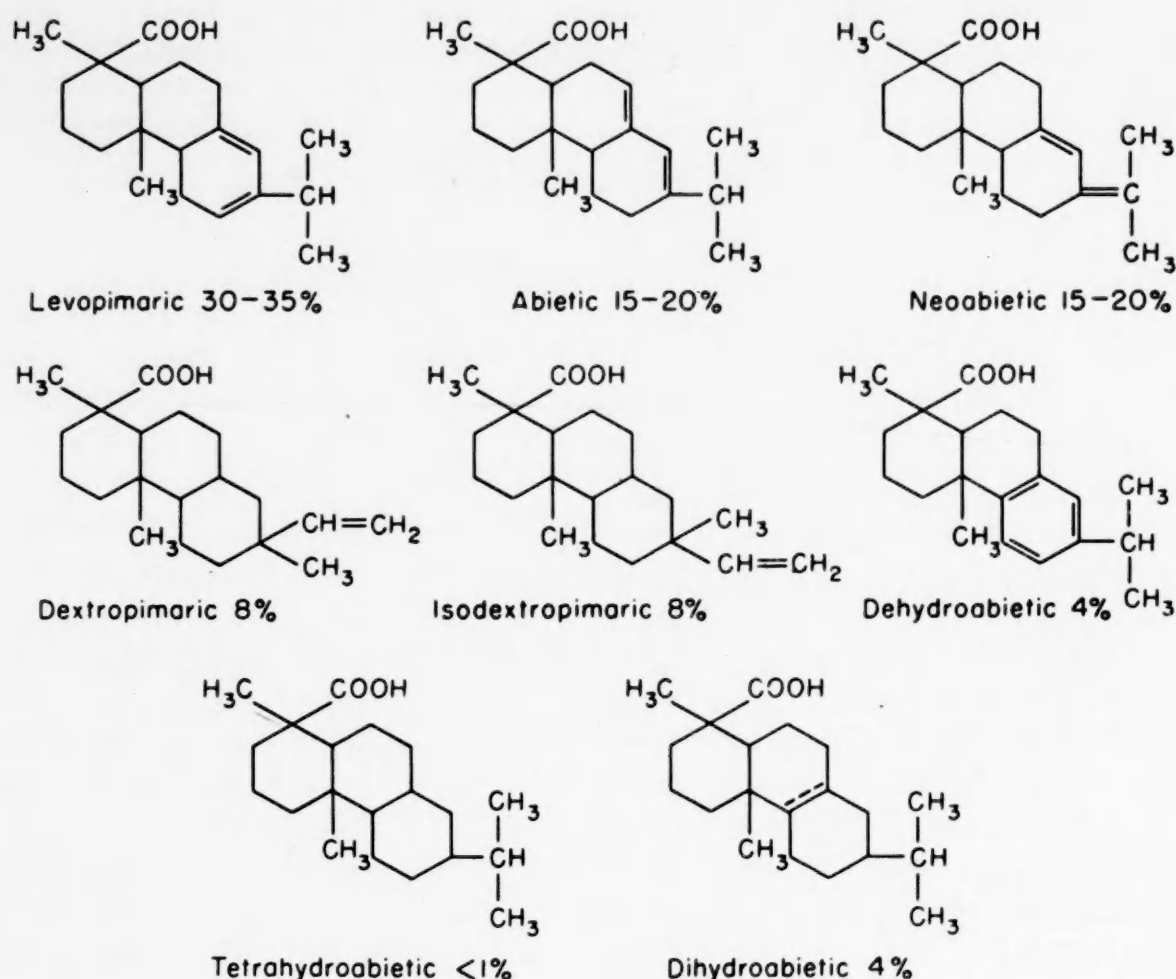# THE RESIN ACIDS

By W. FRANK FOWLER, JR.*

Four genera of coniferous trees (*Pinus*, pine; *Picea*, spruce; *Larix*, larch; *Pseudotsuga*, Douglas fir), all of which include species native to the United States, normally contain horizontally and vertically aligned structures called resin canals, which secrete oleoresin (1). There are four species of southern pine which have been used as commercial sources of the resinous material, but the bulk of the supply now comes from the two found along the Gulf of Mexico, slash pine (*Pinus caribaea*) and longleaf pine (*Pinus palustris*). Although varying somewhat from sapwood to heartwood and from species to species, the trunks of these trees will contain from 4 to 5% of oleoresin. Periodically scraping away small strips of the bark of the trees greatly increases the flow and serves as the basis of an extensive industry in the Southern States and abroad, since this is the source of oleoresin, the residue from turpentine evaporation. The aged stumps of these same softwoods often contain as high as 22% of wood rosin which is extracted with solvents on a commercial scale. In the sulfate and soda processes for producing paper-making pulp, soap skimmings are obtained which, on acidification, yield *tall oil*, a mixture containing approximately 45% of resin acids, 45% of fatty acids, and 10% of neutral material (2). Recently, a method has been devised for the sharp separation of the resin acids in tall oil from the remainder, the process having as its basis the precipitation of these acids as insoluble, crystalline cyclohexylamine salts. These three sources provide an enormous supply of mixed resin acids.

For a good many years, it was thought that resin acids were composed largely of abietic acid. Although abietic acid does comprise an appreciable percentage of the mixture, the researches of Harris and his collaborators (3) have revealed the presence of several related acids. His efforts have resulted in the first truly definitive characterization of the resin acids, a mixture of monocarboxylic acids based on alkylated hydrophenanthrene nuclei. Until these studies were made, tedious and inaccurate fractional crystallizations of the mixed salts of alkali metals were employed in efforts to isolate and define the structures of the component acids of the mixture, oleoresin. Harris discovered that the various acids exhibit a remarkable specificity in reacting with certain amines to form highly insoluble salts. This is the basis upon which he was able successfully to separate these otherwise very similar acids.

The methods which are ordinarily used to separate and characterize solid organic compounds, such as melting point and elementary analysis, are useless here. Addi-

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tion of maleic anhydride to certain of the acids, plus the amine salt technique referred to above, is used to separate these substances. Ultraviolet absorption spectra and optical rotation are employed to characterize them. By using these devices, the resin acids formed in the gum oleoresin of longleaf pine (*Pinus palustris*) have been determined for the first time. These may be found listed below, together with the approximate percentage present in the mixture.

Levopimaric 30-35%   Abietic 15-20%   Neoabietic 15-20%

Dextropimaric 8%   Isodextropimaric 8%   Dehydroabietic 4%

Tetrahydroabietic <1%   Dihydroabietic 4%

In a summary of this kind, detailed discussion of structural proofs is impossible. The interested reader is referred to the Fiesers' excellent review (4). In gum and wood rosins, the same substances are present although the relative amounts are different.

Three of the resin acids contain a conjugated system of double bonds, possess an isopropyl or an isopropylidene group at C-7, and are referred to as abietic-type acids. Levopimaric acid is readily isolated from oleoresin in 20% yield by precipitation from the mixture of acids as its very insoluble butanolamine salt. A weak acid is used for regeneration. Abietic acid is similarly isolated as its diamylamine salt. Neoabietic acid is more difficult to isolate, but this can be accomplished by preparation of the diethylamine salts of the acid mixture. These salts are recrystallized and decomposed, and butanolamine salts are prepared; these latter are recrystallized until a very high positive rotation is obtained and then the pure neoabietic acid is liberated.

One of the abietic-type acids, neoabietic acid, can be isomerized to abietic acid in the presence of hydrogen ion. Abietic acid, in turn, can be isomerized to levopimaric acid by heating at 100°C. Levopimaric acid, even at room temperature, quantitatively undergoes a typical Diels-Alder addition reaction with maleic anhydride, yielding the tricarboxylated product, maleopimaric acid:
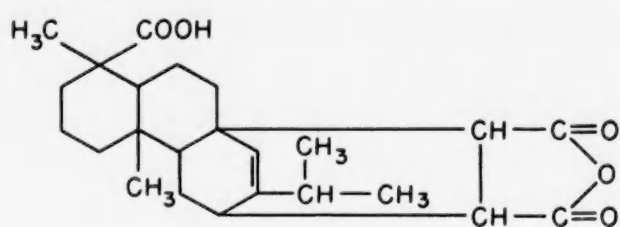
Maleopimaric acid

Thus, gum oleoresin may be heated moderately in the presence of a trace of hydrogen ion and maleic anhydride to yield an amount of the Diels-Alder adduct far in excess of that attributable to the initial presence of levopimaric acid. Maleopimaric acid readily crystallizes from the mixture and can be used, under the conditions specified above, as a means of separating the conjugated from the unconjugated acids.

Treatment of the abietic-type acids with sulfur or preferably selenium at elevated temperature yields the same interesting aromatic hydrocarbon, retene (4).
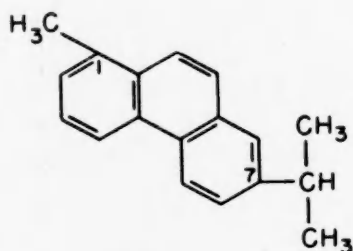
Retene

This substance, 1-methyl-7-isopropylphenanthrene, is a useful intermediate in the synthesis of physiologically active substances. Numerous derivatives, difficult to synthesize by other routes, have been described, and an excellent review of the literature up to 1939 has been published (5). Dehydrogenation of abietic-type acids to yield retene, once Bucher (4) had established its structure, proved to be of major importance in elucidating the structures of this group of resin acids.

Aside from the lack of a conjugated system of double bonds, the so-called pimaric-type acids have a gem configuration involving a methyl and a vinyl group at C-7. When they are dehydrogenated in a manner similar to that used with the abietic-type acids, pimanthrene (1,7-dimethylphenanthrene) results. Like retene, pimanthrene serves as a useful intermediate for the synthesis of a variety of other substances of biological interest. The pimaric-type compounds include dextropimaric acid and isodextropimaric acid, which do not exhibit absorption in the ultraviolet region because of the lack of conjugation of their double bonds. These acids are separated from rosins by distillation as more volatile constituents, and are separated from one another by utilizing the extreme insolubility of the butanolamine salt of isodextropimaric acid.

Dehydroabietic acid, containing three instead of two double bonds—all in one ring—exhibits reactivity characteristic of an aromatic compound. For example, this substance can very readily be sulfonated, yielding the crystalline sulfonic acid; or the methyl ester can be treated with acetyl chloride in nitrobenzene, in the presence of aluminum chloride, to produce the 6-acetyl derivative (6). Pure synthetic dehydroabietic acid was prepared by oxidation of abietic acid with selenium dioxide to the 6-hydroxy derivative followed by dehydration. This substance had an absorption spectrum characteristic of compounds containing one aromatic ring.

When dihydroabietic acid is treated with sulfuric acid, it forms a lactone, which is insoluble in alkaline solutions but soluble in organic solvents. In this way, it can be separated from the other acids. While only present to the extent of about 4% in the oleoresin, obtained from the tree exudate, it accumulates in older stump wood to the extent of 14%. Dihydroabietic acids are less susceptible to oxidation than those containing more than one double bond.

The completely saturated (and therefore very stable) tetrahydroabietic acids are only present in minute amounts in oleoresin but may appear to the extent of 14% in old stump wood. Careful studies have shown that, as the acids age in the tree, they are converted both to the dihydro- and the tetrahydroabietic acids at the expense of levopimaric acid, which is only present in minute amounts in the resin acid mixture obtained from old stumps. Once the abietic-type and the pimaric-type acids are removed from a given natural mixture, tetrahydroabietic acids can be collected separately by treatment with concentrated sulfuric acid at 0°C. On such exposure, the dehydroabietic acid, which is also present, forms the sulfonate (soluble in aqueous sodium bicarbonate), whereas the dihydroabietic acids lactonize and are only soluble in the organic solvent. Tetrahydroabietic acids are extracted with sodium hydroxide.

The changes brought about in the structure of abietic acid by heat are different, depending upon the temperature and the catalyst. When it is heated for 20 minutes at 300°C in the absence of catalyst, some neoabietic acid is formed (5). On the other hand, heating abietic acid at 245°C for one hour in the presence of palladium charcoal results in a complicated disproportionation reaction (4) from which dehydroabietic acid, a tetrahydro acid, the known lactone of hydroxytetrahydroabietic acid, and a dihydroabietic acid have been isolated. Practical use of the disproportionation reaction is made in the preparation of special rosin soaps (7) for employment as emulsifiers in the copolymerization of butadiene and styrene to manufacture synthetic rubber. For this use, it is necessary to remove phenolic inhibitors by suitable refining and abietic-type acids by disproportionation.

Stability of the resin acids to air and light is related to the nature of the unsaturations found in the acid. Oleoresin itself is colorless when freshly collected from the trees, but assumes a brown color on standing in the air. Experimentally, it has been established that the respective pure acids respond in different ways to oxygen, depending upon the structure of the acid, the presence and quality of radiant energy, and the nature of the diluent, if any. The abietic-type acids are readily oxidized by air in benzene, abietic acid itself absorbing two moles of oxygen, while levopimaric absorbs one (8). In the latter case, a transannular peroxide probably forms.
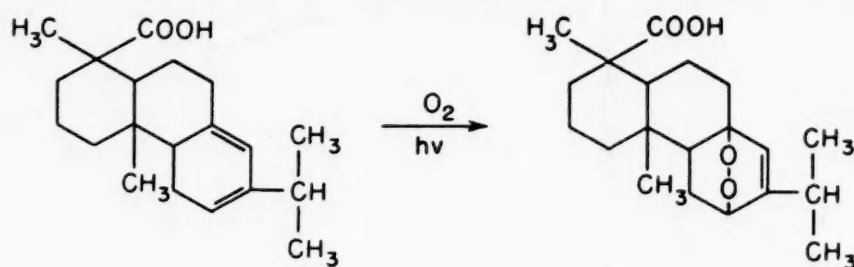
The fact that peroxides do form has been established (9); that these may be of the type shown above is indicated by the disappearance of double bonds. Bachman and co-workers (10) oxidized abietic acid in ethanol solution using unfiltered ultraviolet light, obtaining a mixture of dihydroxy- and tetrahydroxyabietic acids. Dextropimaric and dihydroabietic acids require pure oxygen to be oxidized. Many attempts have been made to stabilize the resin acids against autoxidation, and the ordinary antioxidants, such as hydroquinone, pyrogallol, and resorcinol, as well as

the zinc, copper, and lead salts of abietic acid, have been found effective (11). However, reduction of the double bonds, though requiring high pressures for complete reaction, is most effective in ensuring color stability.

From the standpoint of commercial application, by far the most important reaction of the resin acids is their salt formation with sodium hydroxide and subsequent coagulation upon papermaking fibers with alum. This is the widely used method of beater-sizing paper in order to increase the water resistance of the finished sheet. Of current interest is the use of a small amount of maleopimaric acid with rosin for sizing, an innovation which markedly improves the efficiency of the rosin-sizing process.

In summary, the more common resin acids have now been positively identified and methods for their isolation in a pure condition perfected. Among the attractions of such substances as starting materials for the synthetic organic chemist are their availability in tremendous quantities from a renewable natural resource, their ready conversion to substances of marked physiological activity, their pronounced hydrophobic character, and the ability of their salts and other hydrophilic derivatives to orient at various interfaces.

References

1. Brown, H. P., Panshin, A. J., and Forsaith, C. C., "Textbook of Wood Technology," McGraw-Hill Book Co., New York, 1949, p. 160.
2. Harris, G. C., "Nature of the Chemical Components of Wood," TAPPI Monograph No. 6, Technical Assoc. of Pulp and Paper Industry, New York, 1948, pp. 167-181.
3. (a) Harris, G. C., and Sanderson, T. F., *J. Am. Chem. Soc.*, 70, 334-339 (1948); *Ibid.*, 70, 339-343 (1948); *Ibid.*, 70, 2079-2081 (1948); 70, 2081-2085 (1948).
   (b) Harris, G. C., and Sparks, J., *Ibid.*, 70, 3674-3675 (1948).
   (c) Harris, G. C., *Ibid.*, 70, 3671-3674 (1948).
4. Fieser, L. F., and Fieser, M., "Natural Products Related to Phenanthrene," 3rd Ed., Reinhold Publishing Corp., New York, 1949, pp. 40-91.
5. Adelson, D. E., and Bogert, M. T., *Chem. Revs.*, 24, 135-176 (1939).
6. Fieser, L. F., and Campbell, W. P., *J. Am. Chem. Soc.*, 60, 2631-2636 (1938).
7. Hays, J. T., Drake, A. E., and Pratt, Y. T., *Ind. Eng. Chem.*, 39, 1129-1132 (1947).
8. Malevskaya, S. S., and Kazeeva, E. V., *Zhur. Priklad. Khim.*, 21, 854-858 (1948); *Chem. Abst.*, 43, 6185 (1949).
9. Pavlyuchenko, M. M., and Pavlyuchenko, K. V., *Lesokhim. Prom.*, 3, 20-24 (1940); *Chem. Leutra.*, p. 1940, Part II (1949-50); *Chem. Abst.*, 36, 6820 (1942).
10. Brown, R. F., Bachman, G. B., and Miller, S. J., *J. Am. Chem. Soc.*, 65, 623-626 (1943).
11. Du Pont, G., and Lévy, J., *Compt. rend.*, 189, 920-922 (1929).

NOTICE

New Analytical Procedures in Which Organic Chemicals Are Used

Abstracts of the following articles are now available from Distillation Products Industries, Eastman Organic Chemicals Dept., Rochester 3, N. Y.

Substance Sought	Eastman Organic Chemical	Reference
Beryllium	P4468 Aurintricarboxylic Acid Ammonium Salt	*Anal. Chem.*, *24*, 1056, 1953
Boron	1179 Curcumin	*Anal. Chem.*, *26*, 418, 1954
Cobalt	P1124 1-Nitroso-2-naphthol-3,6-disulfonic Acid Disodium Salt	*Anal. Chem.*, *25*, 1830, 1953
Copper	6183 2,2'-Biquinoline	*Anal. Chem.*, *25*, 655, 1953
	2596 Diethyldithiocarbamic Acid Sodium Salt	*Anal. Chem.*, *25*, 655, 1953
	2596 Diethyldithiocarbamic Acid Sodium Salt	*Anal. Chem.*, *24*, 1894, 1952
Cyanides	1397 3-Methyl-1-phenyl-5-pyrazolone	*Anal. Chem.*, *25*, 446, 1953
Fluorides	1051 3-Alizarinsulfonic Acid Sodium Salt	*Anal. Chem.*, *25*, 1741, 1953
Hormones	1866 2,4-Dinitrophenylhydrazine	*J. Biol. Chem.*, *201*, 279, 1953
Iron	3289 1,10-Phenanthroline	*Analyst*, *76*, 715, 1951
Isonicotinic Acid Hydrazide	1372 1,2-Naphthoquinone-4-sulfonic Acid Sodium Salt	*Anal Chem.*, *25*, 814, 1953
Ketosteroids	99 *m*-Dinitrobenzene	*Lancet*, p. 586, 1951
Magnesium	3289 1,10-Phenanthroline	*Analyst*, *76*, 715, 1951
Manganese	1088 2,4-Pentanedione	*J. Am. Chem. Soc.*, *73*, 4416, 1951
Molybdenum	2249 Mercaptoacetic Acid	*Anal. Chem.*, *25*, 1363, 1953
Pantothenic Acid Calcium Salt	4408 2,7-Naphthalenediol	*Anal. Chem.*, *25*, 1192, 1953
Sugars	4023 Aminoguanidine Sulfate	*Anal. Chem.*, *25*, 826, 1953
Uranium	2197 1,3-Diphenyl-1,3-propanedione	*Anal Chem.*, *25*, 1200, 1953
	794 8-Quinolinol	*Anal. Chem.*, *25*, 1369, 1953
Vanadium	82 Cupferron	*Anal. Chem.*, *25*, 1863, 1953
Zirconium	6748 *o*-(2-Hydroxy-3,6-disulfo-1-naphthylazo)benzenearsonic Acid Disodium Salt	*Anal. Chem.*, *25*, 1331, 1953

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